PATENT SPECIFICATION

DRAWINGS ATTACHED

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935,432

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International Classification:—**B01d.**

COMPLETE SPECIFICATION

Improvements in the Manufacture of Crystalline Substances

I, THE MINISTER OF AVIATION, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improvements in the manufacture of crystalline substances and provides a process for the size enlargement of crystalline particles whose solubility is dependent upon temperature.

According to the invention, a process for enlarging the size of crystalline particles of a substance comprises maintaining a suspension of variously-sized particles of the substance in a saturated solution of the substance in a solvent in which its solubility is temperature dependent, and subjecting the suspension to repeated temperature cycles during which the substance remains only partially dissolved in the solvent between a first temperature limit at which the substance is less soluble and a second temperature limit at which it is more soluble, whereby smaller particles are completely dissolved as the temperature cycles towards the second limit and the remaining particles are enlarged in size as the temperature cycles towards the first limit.

As a result of each temperature cycle the number of crystalline particles in suspension is reduced and their average size increases. This is because, considering the more usual case in which solubility increases with increase in temperature, during the part of each cycle when there is a rise in temperature the smallest particles tend to dissolve and during the remaining part of each cycle when the temperature falls material thrown out of solution tends to form on the remaining particles rather than form new particles.

In general, it is preferable to avoid substantial further nucleation during a temperature cycle from a more soluble to a less soluble temperature so that the maximum increase in crystal size is obtained. This may normally be achieved by ensuring that the rate of formation of fresh crystalline substance during the part of a temperature cycle from a more soluble to a less soluble temperature does not exceed the rate at which growth on the surface of crystals already present can take place. As there is no comparable limitation on the rate of increase of temperature from the less soluble to the more soluble temperature, in accordance with a feature of the invention, the duration of the process is reduced by making the period of the cycle from the less soluble to the more soluble temperature less than (say about one half of) the period of the preceding cycle from the more soluble to the less soluble temperature. Each complete heating and cooling cycle in general lasts for 3 to 20 minutes, depending upon the rate of crystal growth.

The number of complete temperature cycles and the temperature range required depends upon the initial and finally required crystal size, the concentration of undissolved material, and the solubility characteristics of the system, that is the solubility of the substance at the upper and lower temperatures. 5—10 temperature cycles and a temperature range between 10° and 50° C. is usual.

For example five temperature cycles over a total period of 2 hours between 28° C. and 34° C in an aqueous acetone solution containing 60% by weight of acetone in a stirred vessel caused the percentage of oxalic acid crystals which passed 200 B.S. mesh to decrease from 26% to 3%. When the temperature cycling was between 20° C and 40° C the fines which passed 200 B.S. mesh decreases from 25% to 4% after five cycles

[*Price* 4*s.* 6*d.*]

in one hour. Stirring without temperature cycling, that is with the temperature controlled at a steady value, brought about no discernable increase in particle size under otherwise similar conditions.

The mean particle size of ammonium perchlorate crystals may be increased from 30 to 300 microns by six temperature cycles between 20° and 50° C using water as solvent.

The temperature cycling process may be carried out in a stirred reaction vessel provided with a heater such as a heating coil and/or jacket and a cooling coil and/or jacket. Conveniently the temperature cycling is carried out by passing a hot liquid or fluid such as steam through the coil and jacket if provided during the heating period and then passing a cold liquid therethrough during the cooling period. The process for the size enlargement of crystals in a controlled manner in accordance with the temperature cycling process and a convenient apparatus in the form of a tubular device for carrying out the process will now be described with reference to the drawings filed with the provisional specification in which:—

Figure 1 is a cross-sectional side view of the tubular device; while

Figures 2 and 3 are histograms each showing the particle size distribution of crystals before and after treatment in the tubular device.

The tubular device shown in Figure 1 consists essentially of two long inclined tubes or pipes T1 and T2 which are connected together through a bent portion. A feed chamber 1 is connected to the input end and a collecting chamber 2 to the output end of the device. The chamber 2 is provided with a pressure-equalising pipe 4 having an overflow outlet 5 just above the outlet of the feed chamber 1. A continuously flowing liquid-solid system may then be maintained in the tubular device by steadily pouring liquid and suspended crystals into the feed chamber 1 at the required flow rate. Liquid is then continuously discharged through the overflow pipe 5 but the collecting chamber 2 is provided with a lower outlet 3 controlled by a stopcock through which crystals which collect in the chamber 2 may be drawn off when desired.

The liquid-solid system in the tubular device is given an oscillatory movement which is superimposed on the otherwise steady onward movement throughout the length of the tubes T1 and T2 by the action of a pulsing unit. This unit consists of a piston P which is driven in a reciprocating manner by a motor M and which acts on the liquid system through a diaphragm D at the bent portion of the main tube.

The tubular device is fully described and claimed in copending patent application No. 17,126/58 (Serial No. 935,431) of which this is a divisional patent application.

For the purposes of the heat cycling process in accordance with the present invention the tubular device is provided with two heating jackets H1 and H2 and two cooling jackets C1 and C2 so that the liquid system passing through the device is heated and cooled and then heated and cooled again. The temperatures of the jackets H1, H2, C1 and C2 are adjusted to give the desired rise and fall in temperature in the liquid system, the oscillatory movement of the liquid ensuring that there is a good heat exchange in and therefore an even temperature in the liquid system.

Before a continuous recrystallising process is commenced, the tubular device is filled with a liquid consisting of a solvent for the substance to be recrystallised and the apparatus is freed of all air pockets. A slurry containing small crystalline particles of the solid in the solvent is supplied to the feed chamber 1 at a steady rate. The pulsing unit is started and the heating and cooling jackets adjusted to give the required temperature conditions in the liquid-solid system.

Some of the crystalline particles, especially the smallest ones dissolve when they pass through the heating jacket H1 so that the number of particles is reduced. When the liquid system reaches the cooling jacket C1 some of the substance in solution will crystallise out but as this recrystallisation takes place principally by enlargement of existing particles, previously reduced in number, the temperature cycling process has the total effect of causing an increase in the mean size of the crystalline particles.

This particle size enlargement is repeated as the liquid-solid system undergoes a second temperature cycle as it passes on through the second heating and cooling jackets H2 and C2. The solids which pass through the tubes T1 and T2 settle in the collecting chamber 2 and are drawn off through the outlet 3 while the clear solvent which is discharged through the overflow pipe 5 may be used to reslurry more solid as required.

The liquid system flow rate, angle of slope of the tubular device, amplitude and frequency of the superimposed oscillation, upper and lower temperature conditions in each temperature cycle and the number of temperature cycles imposed on the liquid system may be varied in order to obtain a desired particle size distribution in the final solid output.

Two examples of a working process for increasing the particle size of a typical crystalline organic substance, oxalic acid, in the tubular device will now be given. In each process the liquid system, which consists of oxalic acid dissolved in cyclohexanone, is taken through six temperature cycles each of 50° C rise and fall, while the initial particle size distribution is, as shown by the lines 20 shown in Figures 2 and 3, as follows:—

20% 0—20 microns diameter
45% 20—40 microns diameter
15% 40—60 microns diameter
20% Over 60 microns diameter

In each process the tubular device consists of a tube having a bore of about 1.2 cms. and the length which runs through one heating and cooling jacket is about 3 metres.

In the first process under these conditions and when the pulsing unit operates at about 200 pulses/min. and about 1 kilogram of the crystals is passed through the six temperature cycles in about 110 minutes the resulting particle size distribution is such that the histogram shown by the line 21 in Figure 2 exhibits a distribution with a peak at about 160 microns diameter in a range from about 50 to 350 microns.

In the second process under the above specified conditions and when the pulsing unit operates at about 55 pulses/min. and about 1 kilogram of the crystalline substance is passed through the six temperature cycles in about 120 minutes, the resulting particle size distribution is such that the histogram is as shown by the line 31 in Figure 3 with a first peak at about 180 microns and a second peak at about 240 microns.

These results shown that under these conditions defined above the tubular device is capable of producing an effect which causes a bimodal final particle size distribution which if suitably adjusted can be made into a fairly even broad distribution. For example, the line 31 in Figure 3 shows that a reasonably even particle size distribution is produced by the second process in the range 125 to 275 microns.

WHAT I CLAIM IS:—

1. A process for enlarging the size of crystalline particles of a substance which comprises maintaining a suspension of variously-sized particles of the substance in a saturated solution of the substance in a solvent in which its solubility is temperature dependent, and subjecting the suspension to repeated temperature cycles during which the substance remains only partially dissolved in the solvent between a first temperature limit at which the substance is less soluble and a second temperature limit at which it is more soluble, whereby smaller particles are completely dissolved as the temperature cycles towards the second limit and the remaining particles are enlarged in size as the temperature cycles towards the first limit.

2. A press according to Claim 1 wherein the period in each temperature cycle in which the temperature cycles towards the first temperature limit exceeds the period in which the temperature cycles towards the second temperature limit.

3. A process for enlarging the size of crystalline particles substantially as hereinbefore described with reference to Figure 1 of the drawings filed with the provisional specification.

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Agent for the Applicants.

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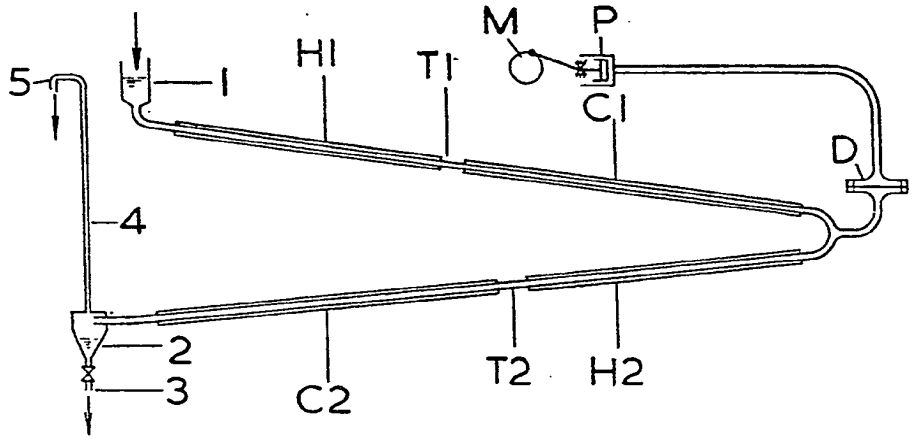


FIG. 1.

935432 PROVISIONAL SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheets 1 & 2

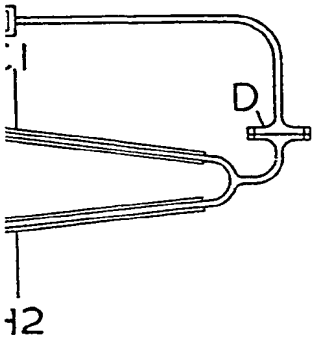


FIG. 2.

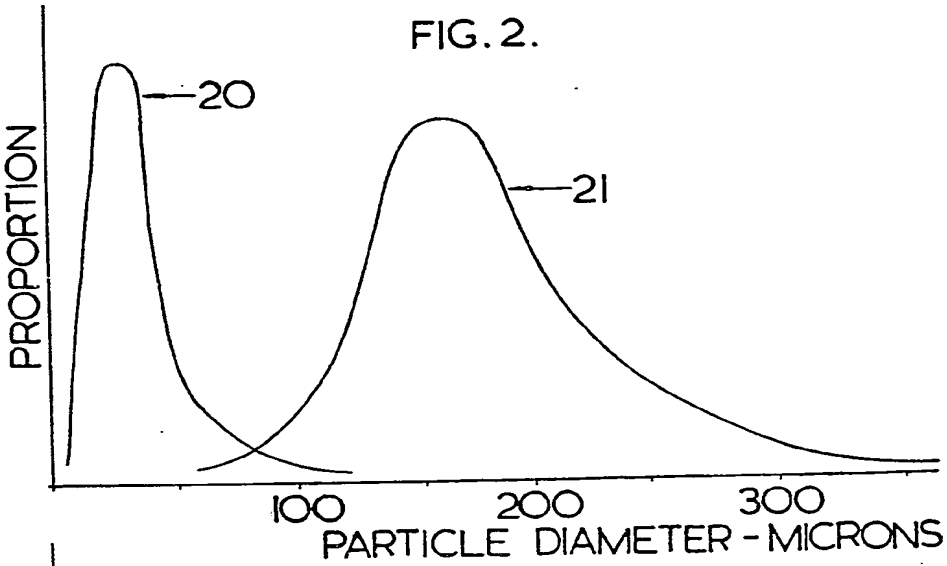
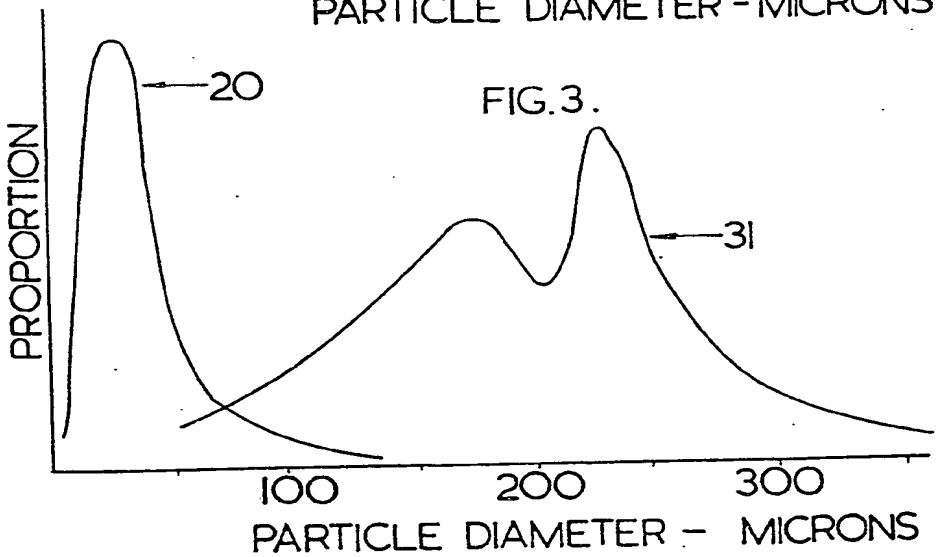


FIG. 3.



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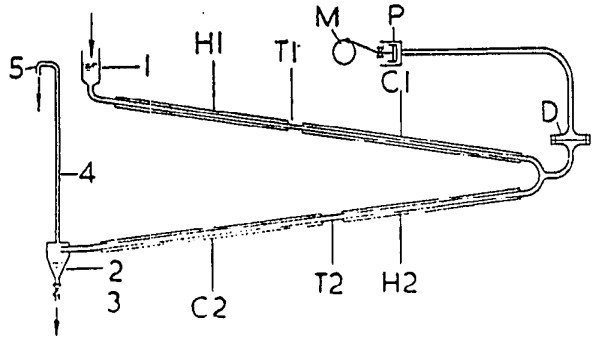

FIG. 1.

FIG. 2.

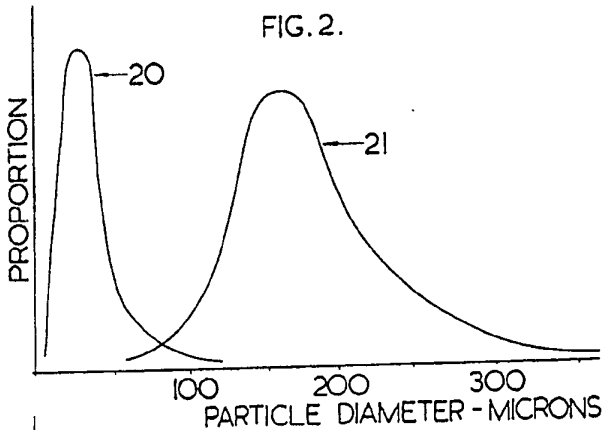

FIG. 3.